LAWRENCE
LIVERMORE
NATIONAL
LABORATORY

Massively Parallel Combined Monte Carlo and Molecular Dynamics Methods to Study the Long-Time-Scale Evolution of Particulate Matter and Molecular Structures Under Reactive Flow Conditions

Alison Kubota, Christopher J. Mundy, William J. Pitz, Carl Melius, Charles K. Westbrook, Maria-Jose Caturla

December 22, 2003

Disclaimer

Massively Parallel Combined Monte Carlo and Molecular Dynamics Methods to Study the Long-Time-Scale Evolution of Particulate Matter and Molecular Structures Under Reactive Flow Conditions

Alison Kubota[*], Christopher J. Mundy, William J. Pitz, Carl Melius and Charles K. Westbrook
Lawrence Livermore National Laboratory, Livermore, CA 94551, USA

Maria-Jose Caturla
Department de Fisica Aplicada Universitat d'Alicant, E-03690, Alicant, Spain

Abstract
An important challenge in computational modeling is the development of new computational methods and capabilities for studying molecular-scale structures over very large time-scales. In particular, there is great interest in understanding the nucleation and growth of carbon soot particles as well as their fate in the atmosphere. We have recently developed and implemented a new computational tool to time-integrate the detailed structure of atomistically resolved surfaces and nanostructures driven by chemical and physical kinetic rule-based rate expressions. Fundamental chemical and physical processes such as chemical reactions, surface adsorption and surface diffusion are performed using a non-lattice real-space kinetic Monte Carlo scheme and driven by user-defined rule-based kinetic rate expressions, while atomic structure relaxation is approached using molecular dynamics. We demonstrate the sensitivity of particle evolution to chemical and physical kinetic mechanism using a parallel implementation of the combined Monte Carlo and molecular dynamics code.

Introduction

It is essential to understand the detailed chemical and physical processes involved in the birth and growth of particulate matter in chemically reactive flow conditions. Of particular interest is the carbon nanoparticulate matter, also called soot, that is formed in automobile engines and in hydrocarbon fuel burning power plants. Soot has been found to be the leading source of cancer risk from toxic air pollution[1]. Soot particles, which typically have aromatic and carcinogenic properties are small enough to evade the body's physical defenses and lodge deep into the lung tissues. Soot also has an essential role in improving the radiative energy transport processes that increase the efficiency of steam furnaces.

Recent approaches have attempted to combine particulate matter chemistry with gas-phase chemistry with the use of lumping or polymerization methods with varying degrees of sophistication. Such a multiscale approach to particulate matter has the expected effect of the loss of detailed information on the particles themselves. However, recent advances in experimental particulate detection and characterization[2] have demonstrated the ability to detect and analyze nanoparticulate soot with unprecedented levels of detail. Thus, it is highly advantageous to have new predictive tools to model the detailed evolution of the soot particles themselves.

We have recently developed at LLNL a new and novel technique of predictively modeling the long timescale evolution of particles and surfaces with atomic-scale resolution. This method and code that we call KMC/MD involves the use of kinetic Monte Carlo (KMC) and classical atomistic simulations to integrate over time, the atomistic-scale structures of arbitrary particles or surfaces that are exposed to a time-varying reactive local environment. For sake of simplicity, we will refer to the classical atomistic simulations as MD, or molecular dynamics. However more generally, numerous other methods can be substituted.

Described individually, MD and KMC are two very different approaches to finding time-integrated solutions to differential equations. MD is a deterministic particle method involving numerical computation to time-integrate the motion of an ensemble of n particles consistent with Newton's equation,

$$\mathbf{F}_i = m_i\, \mathbf{a}_i = -\nabla V(\mathbf{q}_1,..,\mathbf{q}_n) \qquad (1)$$

It is the interatomic potential, $V(\mathbf{q}_1,..,\mathbf{q}_n)$ or the force fields, $\mathbf{F}_i$ that defines the energy landscape over which trajectories will traverse. MD involves discretizing Equation (1) separated into two first-order ordinary differential equations over the phase space, $(\mathbf{p}_i, \mathbf{q}_i)$ over timescales on the order of picoseconds.
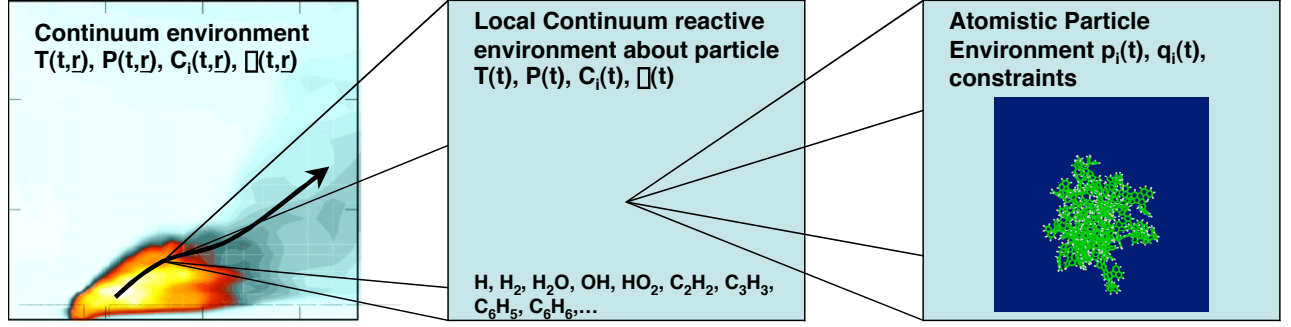

Figure 1: The multiscale nature of nanoparticulate growth under reactive flow conditions. In the KMC/MD formulation, the spatial scales are assumed to be decomposed into three different length scales: (a) the continuum macroscopic environment, (b) the quasi-Lagrangian locally homogeneous environment, and (c) the atomistic particle environment.

KMC, on the other hand is a stochastic method involving the numerical integration to find the time-integrated solutions that are consistent with the Master equation,

$$dP_\alpha/dt = \sum_\beta W_{\beta\to\alpha} P_\beta - W_{\alpha\to\beta} P_\alpha, \qquad (2)$$

where $W_{\alpha\to\beta}$ are state-to-state transition probabilities per unit time from state α to state β, and P_α is the probability of finding the state in configuration α. These state-to-state transitions, which we also refer to as "reactions" for simplicity, are probabilistically weighted according to a user-defined "kinetic mechanism." This mechanism consists of kinetic rates and parameters of all possible physical and chemical processes such as particle surface reactions and surface diffusion and adsorption processes.

KMC/MD Methodology

Figure 1 shows the general framework in which the KMC/MD formulation is applicable. Figure 1(a) represents the reactive-macroscopic flow field in which soot particles are formed in. We assume that each

discrete particle is always in a quasi-Lagrangian time-dependent and homogeneous local environment, as shown in Figure 1(b). This single discrete particle is additionally allowed to "exist" computationally with full atomistic detail, as shown in Figure 1(c). An analogous description following a single particle precursor in time and space. As it travels through different reactive conditions, the particle "sees" a changing physical and chemical environment which thus influences the rates of the physical and chemical processes occurring on the particle.

The coupling in Figure 1(a)-(c) embodies the KMC/MD methodology. In KMC/MD, the two major features are that (1) atomic level detail for a single structure is arbitrary without having to occupy rigid lattice positions, and (2) these structures evolve due to the physical and chemical kinetic processes such as surface reaction and diffusion, defined as an input to the computational simulations. Thus, all forward and reverse transition processes need to be defined explicitly.

Figure 2 shows in more detail how KMC/MD works in terms of the flow of information. Unlike the usual multiscale modeling methods, information passes both ways between the deterministic and stochastic integrators.
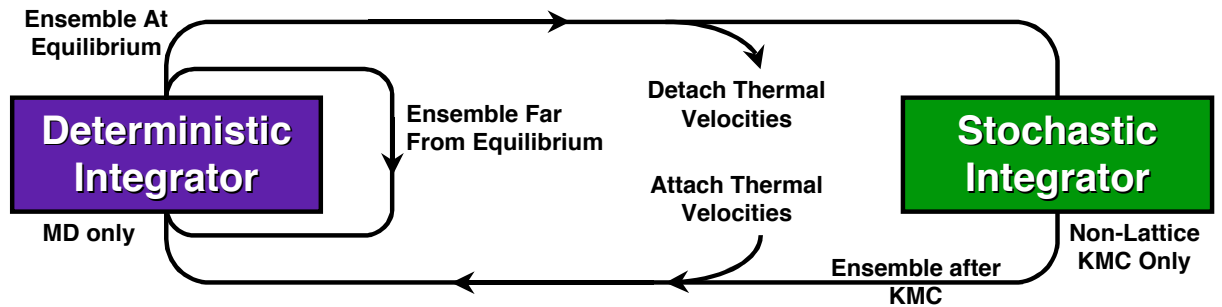

Figure 2: The flow of information in the KMC/MD formulation. During a single KMC/MD iteration, a particle configuration is first modified by the stochastic integrator on the right. Thermal velocities are then added to produce the full phase space that is then equilibrated by the deterministic integrator on the left. After the particle configuration has been brought to thermal and structural equilibrium, only the configuration space is then passed to the stochastic integrator.

$$R(t) \ (1/\text{sec}) = k(T(t), P(t), \mu(t)) \ C_i(t) \ N_{\text{site}}$$

Local Continuum reactive environment about particle $T(t), P(t), \mu(t), C_i(t)$

H, H_2, H_2O, OH, HO_2, C_2H_2, C_3H_3, C_6H_5, C_6H_6,...

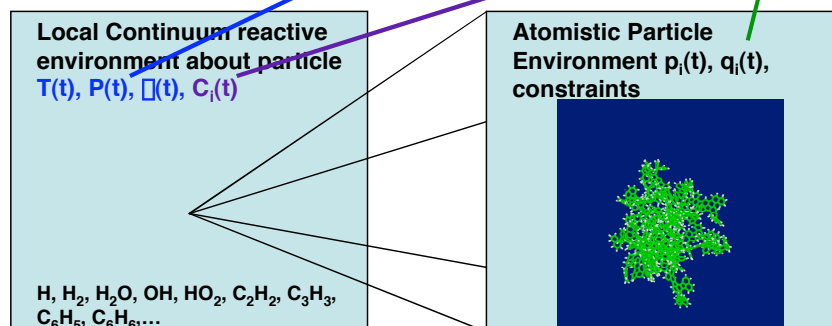**Atomistic Particle Environment** $p_i(t)$, $q_i(t)$, **constraints**

Figure 3: The local continuum environment and atomistic particle environment relative to the kinetic rate in the KMC/MD formulation one particular type of reaction, e.g. gas-surface elementary reaction. In this example, the rate constant is a function of an arbitrary time-dependent pressure and temperature and other arbitary parameters μ that are calculated from the local continuum reactive environment. The gas-phase concentrations c(t) are also taken from this environment. Surface reaction sites are "counted" in the atomistic particle environment.

In a single iterative step, a particle configuration is first passed through the stochastic integrator in which a transition reaction is selected from a menu of reactions. The configuration is then modified according to reaction definitions before being passed to the deterministic integrator. The configuration is then brought to equilibrium using various constraint and thermostat procedures. It should be noted that the information bandwidth into and out of the deterministic and stochastic integrators are different, with the stochastic integrator requiring only the configuration space, and the deterministic integrator requiring both the momentum and configuration space.

Figure 3 shows the roles of the different environments shown in Figure 1 to the KMC/MD algorithm. To calculate a single Monte Carlo time-step iteration, it is first required to tabulate all configuration "states" and state-to-state transition probabilities. In the language of surface chemistry, this corresponds to "tabulating all surface reaction sites and surface reaction rates." For any particular gas-surface elementary reaction, one can assume a rate that goes as

$$\text{Rate (sec}^{-1}) = k(T(t), P(t), \mu(t)) \ C_i(t) \ N_{\text{site}} \quad (3)$$

Where $k(T(t), P(t), \mu(t))$ is the kinetic rate constant that has arbitrary and user-defined dependences on temperature, pressure, and any other definable parameters $\mu(t)$). $C_i(t)$ correspond to the gas-phase concentration at the particle surface. These quantities are derived from the locally homogeneous environment variables in Figure 2. N_{site} however, is the number of reactive sites for that transition, and is dependent on the atomic structure during

a particular iteration. The criteria for site counting and the descriptions for performing particular transitions are also defined in the simulation input, and we present some specific examples further.

Code Implementation

The current implementation of a massively parallel KMC/MD code at Livermore was based around systems containing Carbon, Hydrogen and Oxygen atoms. The KMC phase of the code was developed around a spatially decomposed framework with strictly O(n) scaling, where n is the number of atoms in the system. Chemical and physical kinetic rate expressions, transition definitions, transition site definitions, and all time-dependent variables such as gas-phase concentration, temperature and pressure are implemented through a precompiler that combines code elements into a single memory-efficient framework. The MD phase of the code was also developed around a spatially decomposed framework also with strict O(n) scaling. Additionally, we developed and implemented Carbon-Hydrogen-Oxygen reactive bond-order potentials[3] that are based on the Carbon-Hydrogen potentials of Brenner[4]. This C/H/O potential includes full bond-order-type cross-terms and is highly parameterized to fit a large database of cluster electronic structure and experimental gas-phase and solid-phase data.

Calculations and Discussion

We performed a number of particle growth trajectory simulations using fictitiously derived sets of reactions and gas-phase conditions to illustrate the following points: (1) the type of timescales that can be spanned with KMC/MD
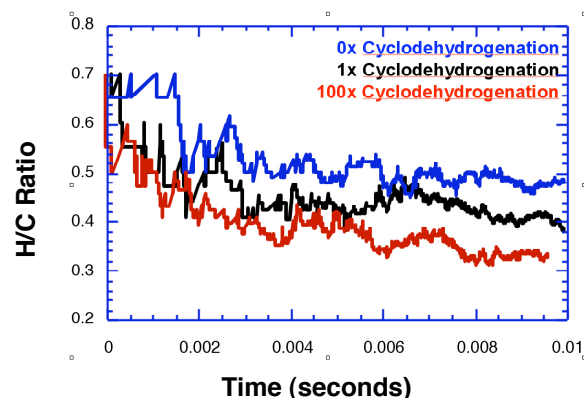
Figure 4: The variation of the cyclodehydrogenation rate on the hydrogen-to-carbon ratio evolution over time.

Figure 5: The variation of the cyclodehydrogenation rate on the particle mass (atomic mass units) over time.

can be on the real macroscopic time-scales, (2) the time-integrated atomistic particles provide a level of detail previously unavailable to traditional chemical-kinetic calculations, and (3) the particle evolution is sensitive to the mechanism included by the user. This last point is an important one that distinguishes KMC/MD as a tool for predicting the different particle structures and compositions to test different chemical and physical kinetic mechanisms.

For simplicity, we assumed all rate constants, on a per-site basis to be constant. All specific details of these calculations will be found elsewhere[5,6]. The reaction classes allowed for this contrived mechanism include H addition, H-abstraction, H-termination, PAH addition, PAH-surface termination and cyclodehydrogenation. Physical processes such as surface adsorption and diffusion were ignored to keep the problems simplified. The stable PAHs included benzene, naphthalene and acenaphthalene. Gas-phase concentrations of H, H_2 and PAH stable and radical species were also assumed to be constant and not a function of the gas-surface reaction rates. It is possible, in the general case to include gas-surface mass and energy transport models for overall self-consistency.

To examine the sensitivity of particle evolution to a single chemical reaction, we performed three simulations: (1) growth with cyclodehydrogenation artificially suppressed, (2) growth with the nominal cyclodehydrogenation rate, and (3) growth with the cyclodehydrogenation rate amplified by a factor of 100. Figure 4 shows the hydrogen-to-carbon ration versus time for the three different simulations performed to approximately 10 msec. It is clear from Figure 4 that there is a strong sensitivity of the H/C ratio to the cyclodehydrogenation rate. This particular reaction is responsible for the release of hydrogen into the gas-phase while closing an aromatic ring-structure at the surface.
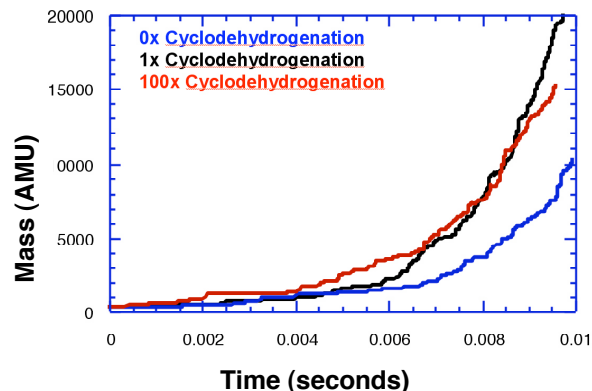
Thus, the high-cyclodehydrogenation rate particle produced the expected result of achieving the lowest hydrogen-to-carbon ratio.

Figure 5 shows the particle mass (in units of atomic mass units) versus time for the three simulations. The very unexpected result is that the particle growth rate for the two simulations with cyclodehydrogenation reactions seems to increase rapidly at 6 msec, compared to the case without cyclodehydrogenation. It may be possible to explain this result in terms of steric conditions that may block certain surface sites from reacting with gas-phase PAH species. More specifically, the cyclo-dehydrogenation reaction leads to the formation of lower-dimensional graphene-like structures, whereas the lack of cyclodehydrogenation forces the particle to grow dendritically. Figure 6 shows the configuration of the particle without cyclodehydrogenation at 6 msec, while Figure 7 shows the particle with amplified cyclodehydrogenation at 6 msec. This dendritic tangle perhaps leads to a reduction in the number of PAH-accessible reaction sites in the non-cyclodehydrogenation case.

Conclusions

We discussed the development and application of the KMC/MD formalism for the atomic scale evolution of soot nanoparticles under reactive flow conditions. We demonstrated that KMC/MD predicts very different nanoparticle evolutionary paths depending on variations in the kinetic mechanism, namely the cyclodehydrogenation reaction rate constant. We believe that further development of KMC/MD as a general tool for particle and surface chemistry will be an invaluable asset to the research community.

Acknowledgements

Berkeley, Professor Michael Zachariah at the University of Minnesota and Dr. Pierre-Alexandre Glaude at CNRS Nancy, France for their very fruitful discussions and comments. We would also like to acknowledge Dr. Angela Violi and Prof. Adel Sarofim for their contributions[7]. This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

References
[1] Associated Press release, South Coast Air-Quality Management District, 2001.
[2] Higgins, K. J., Jung, H. J., Kittelson, D. B., Roberts, J. T. and Zachariah, M. R., *J. Phys. Chem. A* **106** (1) 96, 2002.
[3] Kubota, A., *In preparation*.(2003)
[4] Brenner, D. W., *Phys. Rev. B*, **42** (15) 9458, 1990.
[5] Kubota, A. Poster presented at the 29th International Symposium on Combustion, July 21-26, 2002.
[6] Kubota, A., *In preparation* (2003)
[7] Violi, A., Kubota, A., Truong, T. N., Westbrook, C. K., Sarofim, A. F., *Proc. Combust. Inst.* **29**, in press (2002).
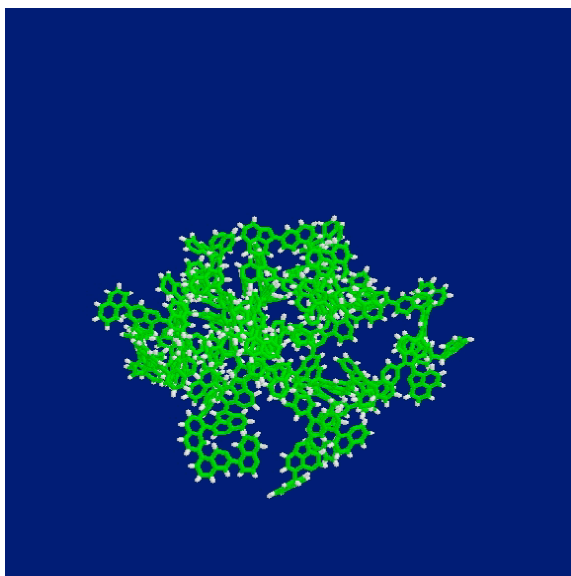
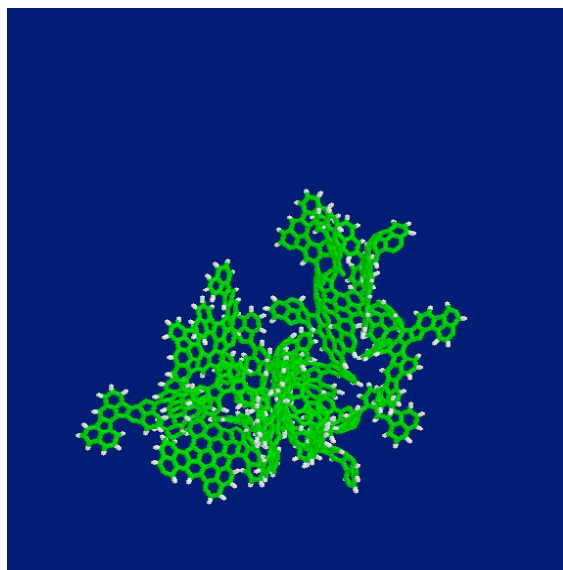Figure 6: Particle at 6 msec without cyclo-dehydrogenation reactions

Figure 7: Particle at 6 msec with amplified cyclo-dehydrogenation reactions